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SELF-DIFFUSION OF METHANOL UNDER PRESSURE

By Hiroyuki Hiraoka, Yasushi Izui, Jiro Osugi and Wasaburo Jono

In the previous reports[1,2], it is indicated that there is no high potential energy barrier for the self-diffusion of benzene because the activation energy at constant volume is as small as 780 cal/mole. The same conclusion was obtained about carbon tetrachloride[3]. It is expected, however, that the activation energy for the self-diffusion of methanol would be large, because for the displacement of methanol molecule the additional energy to surpass the hydrogen bond is required. The self-diffusion coefficients of alcohols at atmospheric pressure reported by Partington *et al.*[4] could not give any precise physical meaning about the effect of temperature on the diffusion rate, because both density and diffusion rate change simultaneously with temperature at constant pressure. The purpose of the present investigation is to know the hydrogen bond effect on the diffusion rate in liquids by conducting the measurements at high pressures.

Experimentals

Materials Radioactive methanol $C^{14}H_3OH$ used as a tracer was purchased from Daiichi Seiyaku Co., Ltd. and the methanol used as a solvent was purified by distillation after the reaction with metallic sodium.

Apparatus and procedures The experimental method used for the measurements up to 1,000 kg/cm^2 was much the same as in the previous reports on the self-diffusion of benzene, except the capillary cell which was about 0.05 ml in volume and about 4 cm in length. The diffusion of methanol at 3,000 kg/cm^2 was performed in the high pressure part of the intensifier[5] which was kept at constant temperature by an air thermostat.

Results

Diffusion coefficients were obtained with the equation (1),

$$\frac{Dt}{l^2}=\frac{4}{\pi^2}\ln\left[\frac{8}{\pi^2}\cdot\frac{C_a}{C_{av}}\cdot\sin^2\frac{\pi}{2}(1-\beta P)\right] \qquad (1)$$

developed in the previous paper.

The results are given in Table 1. The values obtained in the present investigation are smaller at low temperatures and larger at high temperatures than those reported by Partington *et al.*.

1) H. Hiraoka, *Bulletin Chem. Soc., Japan*, 32, 423 (1959)
2) H. Hiraoka, Jiro Osugi and Wasaburo Jono, *This Journal*, 28, 52 (1958)
3) H. Watts, B. J. Alder and J. H. Hildebrand, *J. Chem. Phys.*, 23, 659 (1955)
4) J. R. Partington, R. F. Hudson and K. W. Bagnall, *J. Chem. Phys.*, 55, 77 (1958)
5) R. Kiyama, *This Journal*, 18, 1 (1944)

Table 1 Self-diffusion coefficients (10^{-5} cm²/sec) of methanol

Pressure kg/cm²	Temperature °C 15	25	40
1	1.84±0.01	2.21±0.02	3.01±0.08
500	——	1.90	2.55±0.05
1,000	1.24±0.01	——	2.07
3,000	1.77±0.01		

The results are diagrammatically shown in Figs. 1 and 2. It is interesting to mention that the

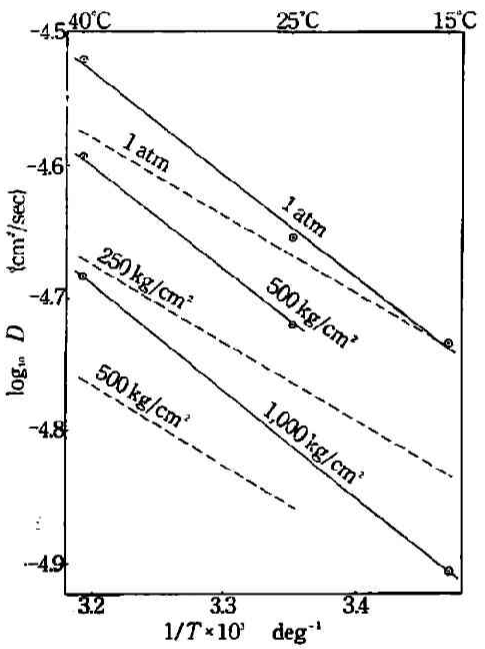

Fig. 1 Self-diffusion coefficients of methanol as a function of temperature in comparison of those of benzene
—⊙— methanol, ----- benzene

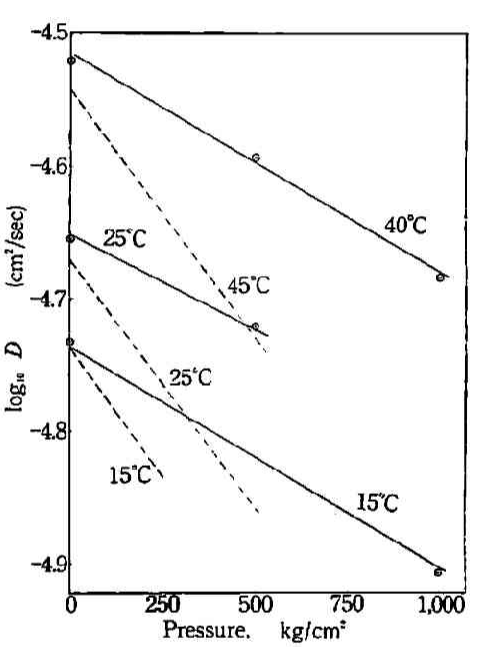

Fig. 2 Self-diffusion coefficients of methanol as a function of pressure in comparison with those of benzene
—⊙— methanol, ----- benzene

pressure effect on the self-diffusion rate of methanol is much smaller than in the case of benzene and the diffusion coefficient of methanol at 3,000kg/cm² is larger than that at 1,000kg/cm².

Discussions

The activation energies at constant pressure for the self-diffusion of methanol computed from the isobars are 3,500cal/mole at 1 atm and 4,000cal/mole at 1,000kg/cm². Methanol has the same molal volume or the same density at 15°C, 1 atm and 40°C, 314kg/cm². Therefore, the activation energy at constant volume is 2,700cal/mole. The activation energy at constant pressure, E_P, is related with the activation energy at constant volume, E_V, by equation (2).

$$E_V = E_{P'} + RT^2\left(\frac{\alpha}{\beta}\right)\left(\frac{\partial \ln D}{\partial P}\right)_T . \qquad (2)$$

The second term on the right of equation (2), $RT^2(\alpha/\beta)(\partial \ln D/\partial P)_T$, is 750 cal/mole. so that E_V at the densities near 1 atm is calculated to be 2,700 cal/mole which is coincident to the experimental value mentioned above and E_V at the densities near 1,000 kg/cm² is 3,200 cal/mole in the temperature range of the present investigation.

The molecular weight of methanol is 41.4% and its molal volume is 45.6% of that of benzene. Therefore, if there is no hydrogen bond in methanol, the activation energy for diffusion should be smaller than that of benzene, but in reality, in order to diffuse the hydrogen bond should be overcome by high translational energy at first. This additional energy causes the high activation energy of methanol 2,700 cal/mole as compared with that of benzene 780 cal/mole.[2] At high densities near 1,000 kg/cm² the potential energy barrier in methanol is intensified, but at far higher densities the effect of the hydrogen bond on the diffusion rate may be neglected and higher diffusion rate is observed at 3,000 kg/cm² as in the self-diffusion of water[6].

The constant value of the quantity, $D\eta/kT$, is required in the theories of diffusion in liquids. The result of the calculation is shown in Table 2, where nearly constant values are obtained up

Table 2 $D\eta/kT(10^{-6}\ \mathrm{cm}^{-1})$ for methanol

Pressure kg/cm²	Temperature 15°C	25°C	40°C
1	2.91	2.97	3.14
500		3.02	3.21
1,000	2.66		3.16

to the pressure range of 1,000 kg/cm². It is expected, however, than macroscopic fluidity $1/\eta$ ceases to be proportional to microscopic fluidity at far higher densities due to the small contribution of the hydrogen bond, and for this reason discrepancy in the values of viscosity and diffusion rate can be observed at pressures as high as 3,000 kg/cm².

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6) R. B. Cuddeback, R. C. Koeller and H. G. Drickamer, *J. Chem. Phys.* **21**, 589 (1953)